

Activity of Ni Substituted Ca-La-hexaaluminate Catalyst in Dry Reforming of Methane

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Abstract $\text{Ca}_{1-x}\text{La}_x\text{NiAl}_{11}\text{O}_{19-\delta}$ ($0 \leq x \leq 1$) hexaaluminate oxides were synthesized starting from nitrate salts of Ca, La, Ni and Al precipitated by citric acid. After calcination they were used as catalysts precursors in dry reforming of methane to synthesis gas at atmospheric pressure (600–800 °C) with a mixture of $\text{CH}_4/\text{CO}_2/\text{Ar}$:1/1/3. The solids were characterized by X-ray diffraction (XRD), BET surface area, temperature programmed reaction and oxidation (TPO) and by X-ray photoelectron spectroscopy. XRD analysis shows a pure hexaaluminate phase as soon as a part of calcium has been substituted by lanthanum. After H_2 reduction and after reactivity test, Ni metal characterized by XRD is responsible of the high activity (equilibrium conversion near 100% at 800 °C). Ni hexaaluminate shows a remarkable high stability (more than 300 h test) probably due to the low formation of surface carbon (TPO).

Keywords Hexaaluminates · Catalyst · Methane · Syn gas

1 Introduction

Natural gas is recognized as one of the fuel of the near future due to the worldwide proven reserve [1]. This situation has produced a growing interest in the development

of technologies able to transform natural gas to liquid energy through the syngas. Dry reforming ($\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$ $\Delta H_{298} = 247 \text{ kJ mol}^{-1}$) produces syngas with a H_2/CO ratio near 1 favourable for Fischer-Tropsch or hydrocarbonylation reactions. Dry reforming could also have environmental implication by the thermochemical valorisation of CO_2 . However, one disadvantage of dry reforming is the accumulation of carbon by methane cracking or CO disproportion over catalytic surface. Coke deposition is strongly influenced by the type of metal used. Noble metals present lower level of coke than nickel [2], however, Ni is generally used because of its low cost and availability [3]. Carbon formation decreases with high nickel dispersion, basic supports, redox promoters [4–6] and also if catalyst presents a strong interaction between nickel and the support. This last feature is obtained when nickel is initially present in a defined structure like perovskite [7], spinel [8], fluorite [9] or in a solid solution (NiO-MgO) [5]. With these structures, metal reduction temperature is increased at a temperature near of the reaction temperature and highly dispersed metallic nanoparticles are produced. The presence of alkali earth or rare earth favours carbonates or oxycarbonates formation and it is well documented that such species react with carbon with CO formation [10].

Hexaaluminates materials $\text{ANiAl}_{11}\text{O}_{19-\delta}$ ($A = \text{La, Ca, Ba, Sr}$) are defined structures, they contain alkali or rare earth oxides and α -alumina has been indicated as preventing coke formation [11]. Consequently they are potential candidates to dry reforming. In fact, $\text{LaNi}_y\text{Al}_{12-y}\text{O}_{19-\delta}$ ($y = 0.3; 0.6; 0.9$ and 1) in which Ni ion is inlaid in hexaaluminate lattice to substitute part of Al ions are of interest and high resistance to carbon deposition and long term stability (300 h) were observed for $\text{La}_{0.8}\text{Pr}_{0.2}\text{NiAl}_{11}\text{O}_{19-\delta}$ [12, 13]. In the present study, a

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series of CaLaNi hexaaluminate were prepared by substitution of Ca by La, characterized and tested in dry reforming of methane in order to investigate the influence of the presence of La in the CaNi hexaaluminate structure on the catalytic dry reforming activity and on the carbon deposition resistance.

2 Experimental

2.1 Catalyst Preparation

The hexaaluminate $\text{Ca}_{1-x}\text{La}_x\text{NiAl}_{11}\text{O}_{19-\delta}$ ($0 \leq x \leq 1$) were prepared as follows: calcium, lanthanum, nickel and aluminium nitrates were dissolved separately in distilled water mixed together to obtain a molar ratio Ca/La/Ni/Al equal to $(1-x)/x/1/11$, respectively. The aqueous solution was slowly added at room temperature to citric acid and heated at 60 °C under stirring to remove excess of water and until formation of a vitreous gel. The gel was then dried at 110 °C overnight and calcined 2 h at 500 °C then 8 h to 1,100 °C.

2.2 Catalyst Characterization

XRD patterns have been obtained using SIEMENS D500 diffractometer ($\text{CuK}\alpha$ radiation : $\lambda = 1.5418 \text{ \AA}$). The obtained phases were determined using fishier ASTM programs (American Society for Testing Material) type DATA FILE PDF Diffraction 2000.

BET surface areas were determined by nitrogen adsorption using Coulter SA 3100 apparatus. Low specific surface areas were obtained ($1\text{--}6 \text{ m}^2 \text{ gcat}^{-1}$, for all samples). Binding energy and chemical composition of surface were measured by XPS (Thermo VG Multilab 2000 using AlK α radiation).

The reducibility of Ni hexaaluminates was studied by TPR and carbon entities formation was determined by TPO as follow: 0.5 g of catalyst was embedded in a quartz reactor (inner diameter 6.6 mm). After purge by argon, the catalyst was heated from room temperature to 900 °C ($15 \text{ }^\circ\text{C min}^{-1}$) in a H_2/Ar mixture ($2/50 \text{ mL min}^{-1}$) for TPR and in a $5/45 \text{ mL min}^{-1}$ O_2/Ar mixture for TPO measurements. In both cases, effluent gas composition was analyzed using TCD gas chromatograph.

2.3 Catalytic Activity Test

CH_4/CO_2 activities were performed in a fixed-bed quartz reactor under atmospheric pressure. 0.05 g of catalyst was first reduced in pure H_2 flow (1 L h^{-1}) at 900 °C, 1 h then purged by Ar and cooled at room temperature for

15 min. Dry reforming gas ($\text{CH}_4/\text{CO}_2/\text{Ar}:1/1/3$; total flow $20 \text{ L h}^{-1} \text{ gcat}^{-1}$) was then admitted at 800 °C temperature. The catalytic activities were investigated between 500 and 900 °C. The reactants (CH_4 and CO_2) and products (CO , CO_2 , H_2) were analyzed on line using TCD gas chromatograph equipped with a Carbosieve column.

3 Results and Discussion

3.1 XRD

Figure 1 shows the XRD patterns of $\text{Ca}_{1-x}\text{La}_x\text{NiAl}_{11}\text{O}_{19-\delta}$ hexaaluminates ($0 \leq x \leq 1$) after calcination at 1,100 °C. For $\text{LaNiAl}_{11}\text{O}_{19-\delta}$ a pure hexaaluminate phase is formed with characteristic diffraction peaks at 36.08; 34.02 and 32.06 (2θ). For $\text{CaNiAl}_{11}\text{O}_{19-\delta}$, we characterize hexaaluminate with low cristallinity, $\alpha\text{-Al}_2\text{O}_3$ and NiAl_2O_4 spinel diffraction peaks localized at 25.3 (2θ) and 37.1 (2θ). In accordance with the literature [14] a A^{3+} cation can promote the formation of Ni hexaaluminate more effectively than A^{2+} cation and as soon few amounts of La^{3+} is added ($x = 0.1$) Ni hexaluminate structure is well crystallized.

As shown in Figs. 2 and 3, the Ni hexaaluminate structure is always present after reduction (until 900 °C) and after dry reforming. After TPR, it is observed at 44.5 (2θ) the characteristic peak of Ni metal. In fact, only a part of the Ni^{2+} of the hexaluminate structure has been reduced to Ni 0 and this will change slightly with the La^{3+} content. In Fig. 3, Ni metal is always present at 44.5 (2θ) and a characteristic peak of carbon at 26.8° (2θ) is evidenced. The intensity of this peak depends of the La content and carbon deposition seems particularly important on $\text{Ca}_{0.7}\text{La}_{0.3}\text{-NiAl}_{11}\text{O}_{19-\delta}$.

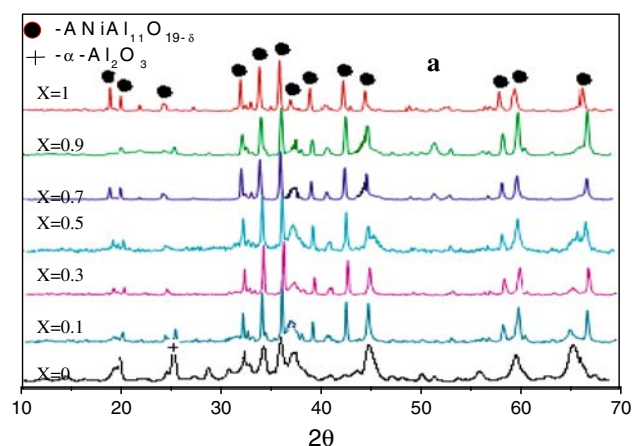


Fig. 1 XRD spectra of calcined $\text{Ca}_{1-x}\text{La}_x\text{NiAl}_{11}\text{O}_{19-\delta}$ structure

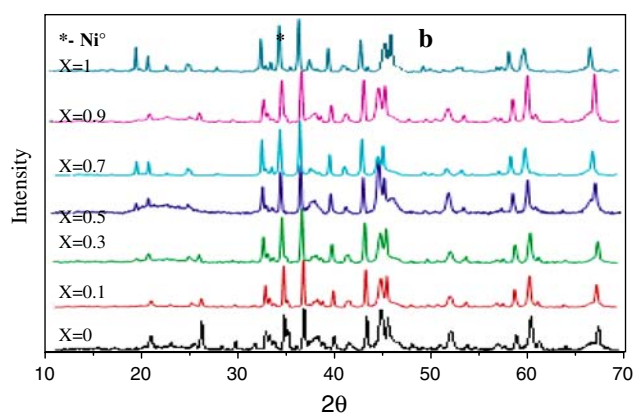


Fig. 2 XRD spectra of $\text{Ca}_{1-x}\text{La}_x\text{NiAl}_{11}\text{O}_{19-\delta}$ after TPR

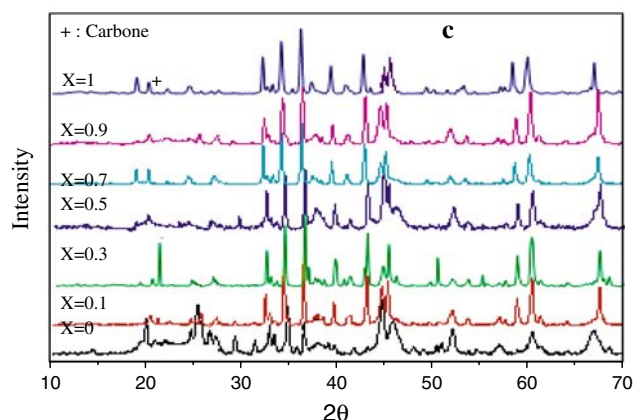


Fig. 3 XRD spectra of $\text{Ca}_{1-x}\text{La}_x\text{NiAl}_{11}\text{O}_{19-\delta}$ after reactivity tests

3.2 TPR

TPR profiles of $\text{La}_{1-x}\text{La}_x\text{NiAl}_{11}\text{O}_{19-\delta}$ catalysts are reported Fig. 4. For all the catalysts, reducibility of Ni is only obtained at very high temperature ($>800^\circ\text{C}$). This clearly indicates that it will be absolutely necessary to reduce all the catalysts before reactivity tests. Maximum of reduction is obtained at nearly 900°C compared to 400°C for NiO [11]. The temperature of the maximum does not change a lot.

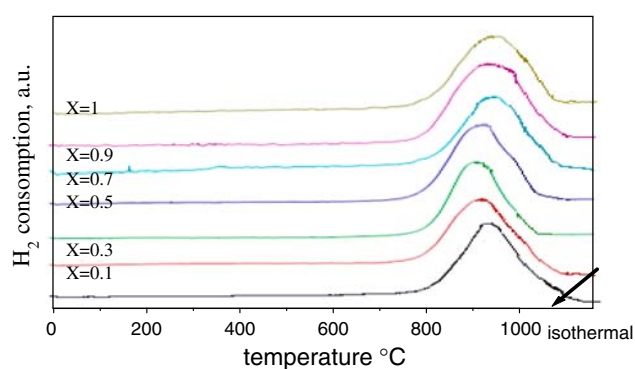


Fig. 4 TPR profiles of $\text{Ca}_{1-x}\text{La}_x\text{NiAl}_{11}\text{O}_{19-\delta}$

However, $\text{Ca}_{0.5}\text{La}_{0.5}\text{NiAl}_{11}\text{O}_{19-\delta}$ is reduced at the lowest temperature. The surface reduction changes also with the content of La. From the evaluation surface area of the hydrogen consumption during TPR, reducibility of $\text{Ca}_{0.5}\text{La}_{0.5}\text{NiAl}_{11}\text{O}_{19-\delta}$ is the highest and has been evaluated at 94% for the nickel. The reduction of the other catalysts has been evaluated between 88 and 92%.

3.3 XPS

The binding energy of the elements of the Ni hexaaluminate is given Table 1. The binding energy of each element is not affected by the Ca substitution by La. For nickel, $\text{Ni}2p_{3/2}$ binding energy of 855.5 eV indicates the presence of nickel into the hexaaluminate lattice in the Ni^{2+} state [15]. La, Ca, Al ions are, respectively, in the 3^+ , 2^+ and 3^+ oxidation states. Table 2 shows the chemical composition at the catalytic surface.

Surface concentrations of La and of Ni are largely lower than nominal composition. This is in accordance with literature data [15, 16]. It is suggested that segregation of Ni is driven by difference in binding energies between the respective elements [17]. The Ni surface concentration increases with the x value for the same reasons. Xu et al. [16] have suggested that the surface Ni concentration correlates with both size and valence of minor cation.

Table 1 Binding energy of surface elements of $\text{Ca}_{1-x}\text{La}_x\text{NiAl}_{11}\text{O}_{19-\delta}$ hexaaluminates

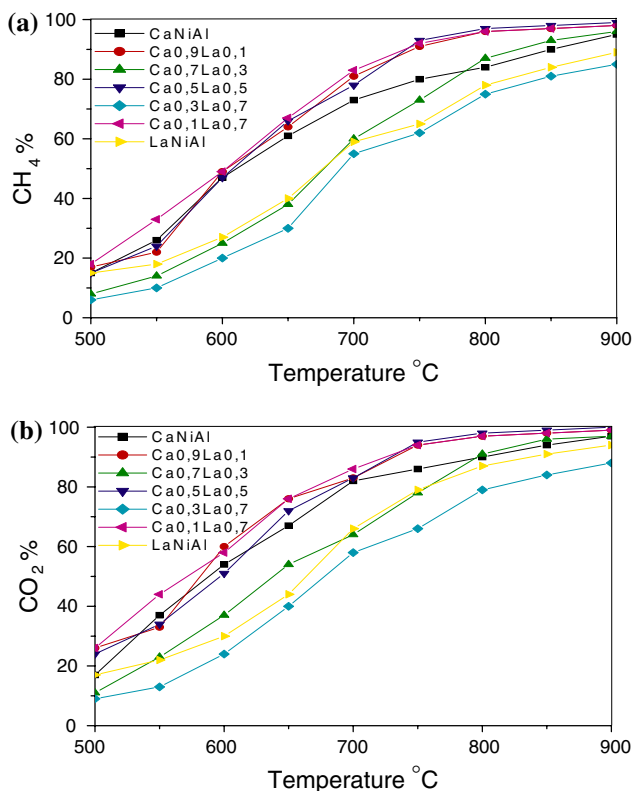
X	Samples	Ca2p _{3/2}	La3d _{5/2}	Ni2p _{3/2}	Al2p	O1s
0	$\text{CaNiAl}_{11}\text{O}_{19-\delta}$	347.1	—	855.2	74.1	530.7
0.1	$\text{Ca}_{0.9}\text{La}_{0.1}\text{NiAl}_{11}\text{O}_{19-\delta}$	347.5	835.2	855.4	74.5	530.9
0.3	$\text{Ca}_{0.7}\text{La}_{0.3}\text{NiAl}_{11}\text{O}_{19-\delta}$	347.5	835	855.5	74.6	531
0.5	$\text{Ca}_{0.5}\text{La}_{0.5}\text{NiAl}_{11}\text{O}_{19-\delta}$	347.5	835	855.5	74.5	531
0.7	$\text{Ca}_{0.3}\text{La}_{0.7}\text{NiAl}_{11}\text{O}_{19-\delta}$	347.4	835	855.5	74.6	531
0.9	$\text{Ca}_{0.1}\text{La}_{0.9}\text{NiAl}_{11}\text{O}_{19-\delta}$	347.2	835	855.3	74.7	531
1	$\text{LaNiAl}_{11}\text{O}_{19-\delta}$	—	835.5	855.3	74.6	531

Table 2 Surface compositions of $\text{Ca}_{1-x}\text{La}_x\text{NiAl}_{11}\text{O}_{19-\delta}$ hexaaluminates (theoretical and as determined by XPS)

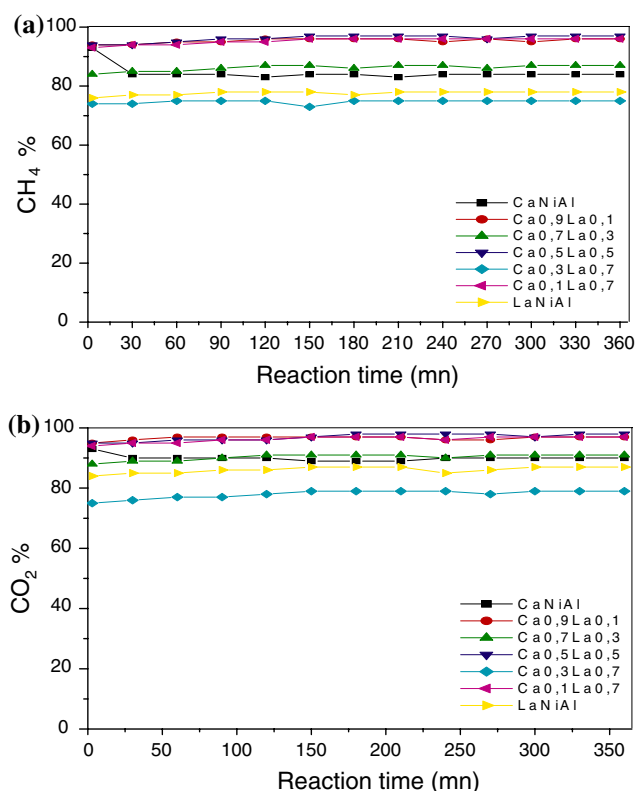
Elements		Ca (%)		La (%)		Ni (%)		Al (%)		O (%)	
X	Samples	Surf	Theor	Surf	Theor	Surf	Theor	Surf	Theor	Surf	Theor
0	$\text{CaNiAl}_{11}\text{O}_{19-\delta}$	5	5.78	—	—	0.9	8.48	44	42.93	50.1	42.81
0.1	$\text{Ca}_{0.9}\text{La}_{0.1}\text{NiAl}_{11}\text{O}_{19-\delta}$	4.43	5.12	0.1	1.97	1.08	8.35	44.15	42.28	50.24	42.28
0.3	$\text{Ca}_{0.7}\text{La}_{0.3}\text{NiAl}_{11}\text{O}_{19-\delta}$	3.85	3.86	0.2	5.75	1.1	8.11	44.57	41.03	50.28	41.25
0.5	$\text{Ca}_{0.5}\text{La}_{0.5}\text{NiAl}_{11}\text{O}_{19-\delta}$	2.72	2.68	0.48	9.32	1.13	7.87	44.1	39.85	51.57	40.28
0.7	$\text{Ca}_{0.3}\text{La}_{0.7}\text{NiAl}_{11}\text{O}_{19-\delta}$	1.9	1.56	0.88	12.68	1.2	7.65	44.1	38.74	51.92	39.37
0.9	$\text{Ca}_{0.1}\text{La}_{0.9}\text{NiAl}_{11}\text{O}_{19-\delta}$	1.04	0.51	1.24	15.86	1.28	7.45	44.5	37.69	51.94	38.49
1	$\text{LaNiAl}_{11}\text{O}_{19-\delta}$	—	—	1.44	17.39	1.6	7.35	45.0	37.19	51.87	38.07

4 Catalytic Activity of $\text{Ca}_{1-x}\text{La}_x\text{NiAl}_{11}\text{O}_{19-\delta}$ Hexaaluminates in Dry Reforming of Methane

The activity of reduced $\text{Ca}_{1-x}\text{La}_x\text{NiAl}_{11}\text{O}_{19-\delta}$ is given Fig. 5 between 500 and 900 °C. No clear correlation was observed between CO_2 or CH_4 reactivity and Ca/La ratio. Even with the low amount of Ni present at the surface (XPS results), all the catalysts present a high activity following thermodynamic data except for $\text{Ca} = 0.3$ and 0.7. Activity is the highest for $\text{Ca}_{0.5}\text{La}_{0.5}\text{NiAl}_{11}\text{O}_{19-\delta}$ which is not the catalyst with the highest content of surface nickel but the catalyst with the highest reducibility (see Table 1).

**Fig. 5** Temperature dependence of catalytic activity over $\text{Ca}_{1-x}\text{La}_x\text{NiAl}_{11}\text{O}_{19-\delta}$

The H_2/CO ratio is always near 1 except for $\text{Ca} = 0.3$. Formation of carbonaceous species is given (Fig. 6) and characterized by TPO. All the catalysts present three main peaks: one is located between 540 and 590 °C. It corresponds to surface carbon deposited as nanotubes on the catalyst. The second one is located between 440 and 455 °C and could be tentatively attributed to carbon located at the vicinity rare earth at of metal and rare earth [18]. It appears like a shoulder of the first one. The third one is located between 330 and 370 °C. Surface area is increasing with the percentage of lanthanum. It could be attributed at the presence of surface carbonates.

**Fig. 6** Peak temperature assignments and total carbon deposited obtained by TPO

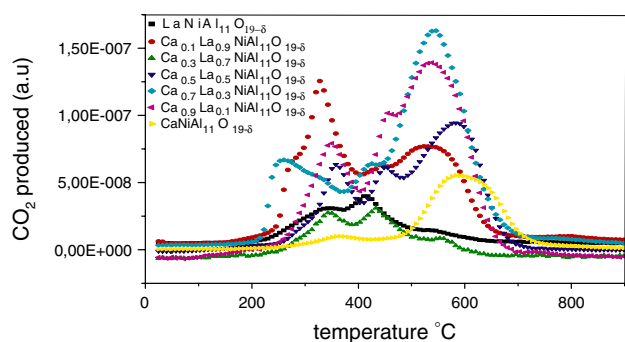


Fig. 7 Stability of $\text{Ca}_{1-x}\text{La}_x\text{NiAl}_{11}\text{O}_{19-\delta}$ catalysts

Finally the stability of the catalysts has been investigated at 800 °C during 6 h (Fig. 7), again $\text{Ca}_{0.5}\text{La}_{0.5}\text{NiAl}_{11}\text{O}_{19-\delta}$ is the most active for CH_4 and CO_2 conversion, $\text{Ca} = 0.3$ given the lowest activity. It should be noticed that in absence of La, the CaNiAl catalyst lost quickly some activity.

5 Conclusion

A series of substituted $\text{Ca}_{1-x}\text{La}_x\text{NiAl}_{11}\text{O}_{19-\delta}$ hexaaluminates were prepared using citric acid method. All the obtained solids have low surface area after calcination at 1,100 °C. As soon lanthanum is present, the formation of hexaaluminate has been confirmed by XRD. After reduction, content of Ni at the catalytic surface is low. However, all the catalysts and more specifically $\text{Ca}_{0.5}\text{La}_{0.5}\text{NiAl}_{11}\text{O}_{19-\delta}$ which has the highest percentage of Ni reduced at the surface (XPS) shows high activity for syngas production but also high stability for the reaction (300 h).

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